PHOTOCATALYTIC REMOVAL OF METHYLENE BLUE USING IMMOBILIZED TRANSITION METALS DOPED TITANIUM DIOXIDE ON GLASS AND GRANULAR ACTIVATED CARBON

KANG LING BAO

SCHOOL OF SCIENCE AND TECHNOLOGY
UNIVERSITI MALAYSIA SABAH
2009

PHOTOCATALYTIC REMOVAL OF METHYLENE BLUE USING IMMOBILIZED TRANSITION METALS DOPED TITANIUM DIOXIDE ON GLASS AND GRANULAR ACTIVATED CARBON

KANG LING BAO

THESIS SUBMITTED IN FULFILLMENT FOR
THE DEGREE OF MASTER OF SCIENCE

SCHOOL OF SCIENCE AND TECHNOLOGY
UNIVERSITI MALAYSIA SABAH
2009

PUMS 99:1

UNIVERSITI MALAYSIA SABAH

BORANG PENGESAHAN TESIS

JUDUL : ____

____

____

IJAZAH : ____

____

SAYA : ______________________ **SESI PENGAJIAN** : ______________________

(HURUF BESAR)

Mengaku membenarkan tesis *(LPSM/Sarjana/Doktor Falsafah) ini disimpan di Perpustakaan Universiti Malaysia Sabah dengan syarat-syarat kegunaan seperti berikut:-

1. Tesis adalah hak milik Universiti Malaysia Sabah.
2. Perpustakaan Universiti Malaysia Sabah dibenarkan membuat salinan untuk tujuan pengajian sahaja.
3. Perpustakaan dibenarkan membuat salinan tesis ini sebagai bahan pertukaran antara institusi pengajian tinggi.
4. Sila tandakan (/)

☐	SULIT	(Mengandungi maklumat yang berdarjah keselamatan atau kepentingan Malaysia seperti yang termaktub di AKTA RAHSIA RASMI 1972)
☐	TERHAD	(Mengandungi maklumat TERHAD yang telah ditentukan oleh organisasi/badan di mana penyelidikan dijalankan)
☐	TIDAK TERHAD	

Disahkan oleh:

______________________ (TANDATANGAN PENULIS)

______________________ (TANDATANGAN PUSTAKAWAN)

Alamat Tetap: ________________

____

____

____

______________________ (NAMA PENYELIA)

TARIKH: ______________

TARIKH: ______________

Catatan:
*Potong yang tidak berkenaan.
*Jika tesis ini SULIT dan TERHAD, sila lampirkan surat daripada pihak berkuasa/organisasi berkenaan dengan menyatakan sekali sebab dan tempoh tesis ini perlu dikelaskan sebagai SULIT dan TERHAD.
*Tesis dimaksudkan sebagai tesis bagi Ijazah Doktor Falsafah dan Sarjana Secara Penyelidikan atau disertai bagi pengajian secara kerja kursus dan Laporan Projek Sarjana Muda (LPSM).

DECLARATION

I hereby declare that this thesis does not incorporate, without acknowledgement; and that the materials in this thesis is my own except for quotations, excerpts, equations, summaries and references, which have been duly acknowledged.

Date: 12/05/2010

KANG LING BAO
PS05-001-019

CERTIFICATION

NAME : **KANG LING BAO**

MATRIC NO. : **PS05-001-019**

TITLE : **PHOTOCATALYTIC REMOVAL OF METHYLENE BLUE USING IMMOBILIZED TRANSITION METALS DOPED TITANIUM DIOXIDE ON GLASS AND GRANULAR ACTIVATED CARBON**

DEGREE : **MASTER OF SCIENCE (INDUSTRIAL CHEMISTRY)**

VIVA DATE : **28th DECEMBER 2009**

DECLARED BY

1. **SUPERVISOR**
   Prof. Dr. Marcus Jopony

2. **CO-SUPERVISOR**
   Assoc. Prof. Dr. How Siew Eng

3. **DEAN OF SCHOOL OF SCIENCE AND TECHNOLOGY**
   Prof. Dr. Mohd. Harun Abdullah

ACKNOWLEDGEMENT

First and foremost, I would like to express my deepest gratitude and appreciation to my supervisor, Prof. Dr. Marcus Jopony and ex-supervisor, Mr. Moh Pak Yan for their patient, all the advices, guidance and support that given in this research work that led to completion of this thesis. I learned a lot, without advices and comments, this thesis will not be as it is.

And special thanks also to my Co-supervisor, Assoc. Prof. Dr. How Siew Eng for her support and advices.

To other Industrial Chemistry lecturers - Dr. Loumie @ Noumie Surugau, Assoc. Prof. Dr. Suhaimi Md. Yasir, Dr. Md. Lutfor Rahman, Dr. Sazmal Effendi Arshad, Mr. Collin G. Joseph, I will be indebted to all of you. The knowledge I gain from you all have shaped me to be different person from I am.

Big thanks also to SST laboratory assistants Mr. Sani Gorudin, Mr. Samudi Suraj, Mr. Mohd. Racyheidy Abd. Rashid, Mr. Mohd. Yusri Jasli, Mrs. Norazima Norbin, thank you for your assistant in the laboratory works and lending the laboratory apparatus.

There are many more names that I don't mention but in some way or other have contributed much to the making of this thesis, whoever they are, I am so ever so grateful for their contribution.

ABSTRACT

PHOTOCATALYTIC DEGRADATION OF METHYLENE BLUE USING IMMOBILIZED TRANSITION METALS DOPED TITANIUM DIOXIDE ON GLASS AND GRANULAR ACTIVATED CARBON

Photocatalytic degradation of methylene blue (MB) dye in aqueous solution using metal-doped titania (TiO_2) under UV-A light and in the presence of H_2O_2 were investigated The photocatalysts used were single metal-doped TiO_2 (i.e. Cr^{3+}-TiO_2, Cu^{2+}-TiO_2, Fe^{3+}-TiO_2, Mo^{5+}-TiO_2, and V^{5+}-TiO_2) and dual metal-doped TiO_2 (i.e. Cr^{3+},Mo^{5+}-TiO_2, Cr^{3+},V^{5+}-TiO_2, Cu^{2+},Mo^{5+}-TiO_2, Cu^{2+},V^{5+}-TiO_2, Fe^{3+},Mo^{5+}-TiO_2 and Fe^{3+},V^{5+}-TiO_2) coated on Pyrex-glass tubes, and single metal doped-TiO_2 (i.e. V^{5+}-TiO_2) coated on granular activated carbon (GAC). All the catalysts were prepared in the lab and the doping/coating was done according to sol-gel dip-coating method. For comparison, undoped TiO_2 coated on Pyrex-glass tube and GAC were also studied. The reactions were carried out in a photo-reactor. Subsamples of the dye solution was withdrawn at specific time intervals and its absorbance was measured at λ_{max}= 665 nm using a UV-Vis spectrophotometer. The resultant dye degradation was presented as % dye removed and comparisons were made for its values at 120 minutes. The results showed that the degradation of MB using these titania-assisted systems increased with reaction time. Equilibrium, however, was not attained within 120 minutes. Amongst the single metal-doped TiO_2 systems only V^{5+}-TiO_2 produced greater degradation of MB compared with the undoped TiO_2. The other single metal-doped TiO_2 systems (Mo^{5+}-TiO_2> Fe^{3+}-TiO_2≈ Cr^{3+}-TiO_2≈ Cu^{2+}-TiO_2) produced much lower degradation compared to undoped TiO_2. For dual metal-doped TiO_2 systems, the degradation efficiency followed the order: Cu^{2+},V^{5+}-TiO_2> Fe^{3+},V^{5+}-TiO_2> Cr^{3+},V^{5+}-TiO_2> Cr^{3+},Mo^{5+}-TiO_2≈ Fe^{3+},Mo^{5+}-TiO_2≈ Cu^{2+},Mo^{5+}-TiO_2. Only Cu^{2+},V^{5+}-TiO_2 produced greater degradation of MB compared with the undoped TiO_2. However, it's efficiency was lower than V^{5+}-TiO_2 but higher than Cu^{2+}-TiO_2. Meanwhile the V^{5+}-doped and undoped TiO_2 catalysts coated on GAC did not exhibit significant photoactivity. The removal of MB from solution by both systems was of similar magnitude to that of due to adsorption by GAC and was about 2x less efficient compared with V^{5+}-TiO_2 and TiO_2 coated on Pyrex-glass tubes. All the above reactions fitted well with pseudo-first-order kinetics according to the Langmuir-Hinshelwood model. Overall, among the systems investigated, photocatalytic degradation of MB is most efficient when V^{5+}-doped TiO_2 coated on an inert support, namely Pyrex-glass tubes, was used.

ABSTRAK

Degradasi fotopemangkinan pewarna metilena biru (MB) dalam larutan akueous telah dikaji dengan menggunakan titania (TiO_2) didopkan dengan logam dalam kehadiran sinaran UV-A dan juga H_2O_2. Fotomangkin yang digunakan adalah TiO_2 yang didopkan dengan logam tunggal (i.e. Cr^{3+}-TiO_2, Cu^{2+}-TiO_2, Fe^{3+}-TiO_2, Mo^{5+}-TiO_2, and V^{5+}-TiO_2) dan TiO_2 didopkan dengan dwilogam (i.e. Cr^{3+},Mo^{5+}-TiO_2, Cr^{3+},V^{5+}-TiO_2, Cu^{2+},Mo^{5+}-TiO_2, Cu^{2+},V^{5+}-TiO_2, Fe^{3+},Mo^{5+}-TiO_2 and Fe^{3+},V^{5+}-TiO_2) dan disalutkan pada tiub kaca Pyrex, dan TiO_2 yang didopkan dengan logam tunggal (i.e. V^{5+}-TiO_2) dan disalutkan pada butiran karbon teraktif (GAC). Kesemua fotomangkin ini telah disediakan di dalam makmal dan pendopan/penyalutan dilakukan secara kaedah sol-gel dip-coating. Sebagai perbandingan, TiO_2 tanpa dopan yang disalutkan pada tiub kaca Pyrex dan GAC juga turut dikaji. Tindak balas degradasi ini telah dijalankan dalam satu reaktor-foto. Subsampel larutan pewarna dikeluarkan pada jangka masa yang tertentu dan serapannya diukur pada λ_{max}= 665 nm dengan menggunakan spektrofotometer UV-Vis. Degradasi pewarna diberikan sebagai % penyingkiran pewarna dan perbandingan nilai dilakukan pada 120 minit. Hasil yang diperolehi menunjukkan bahawa degradasi MB bagi sistem-sistem titania ini meningkat dengan masa tindak balas. Walau bagaimanapun, keseimbangan tidak tercapai dalam masa 120 minit. Di antara sistem-sistem TiO_2 yang didopkan dengan logam tunggal, hanya V^{5+}-TiO_2 menghasilkan degradasi MB yang lebih tinggi berbanding dengan TiO_2 tanpa dopan. Sistem-sistem TiO_2 yang didopkan dengan logam tunggal yang lain (Mo^{5+}-TiO_2> Fe^{3+}-TiO_2≈ Cr^{3+}-TiO_2≈ Cu^{2+}-TiO_2) menunjukkan degradasi yang lebih rendah berbanding dengan TiO_2 tanpa dopan. Bagi sistem-sistem TiO_2 yang didopkan dengan dwilogam, keberkesanan degradasi adalah mengikut urutan: Cu^{2+},V^{5+}-TiO_2> Fe^{3+},V^{5+}-TiO_2> Cr^{3+},V^{5+}-TiO_2> Cr^{3+},Mo^{5+}-TiO_2≈ Fe^{3+},Mo^{5+}-TiO_2≈ Cu^{2+},Mo^{5+}-TiO_2. Hanya Cu^{2+},V^{5+}-TiO_2 menghasilkan degradasi MB yang lebih tinggi berbanding dengan TiO_2 tanpa dopan. Walau bagaimanapun, keberkesanannya adalah lebih rendah daripada V^{5+}-TiO_2 tetapi lebih tinggi daripada Cu^{2+}-TiO_2. Sementara itu, fotomangkin TiO_2 yang didopkan dengan V^{5+} dan TiO_2 tanpa dopan disalutkan pada GAC tidak menunjukkan aktiviti-foto yang signifikan. Penyingkiran MB dari larutan oleh kedua-dua sistem mempunyai magnitud yang sama dengan yang disebabkan oleh jerapan GAC, dan keberkesanannya adalah 2x lebih rendah berbanding dengan V^{5+}-TiO_2 and TiO_2 yang disalutkan pada tiub kaca Pyrex. Kinetik tindak balas diperolehi di atas mematuhi tertib tindak balas pseudo pertama mengikut model Langmuir-Hinshelwood. Secara keseluruhannya, degradasi fotopemangkinan MB dengan menggunakan sistem titania adalah paling berkesan apabila TiO_2 didopkan dengan V^{5+} dan disalutkan pada bahan sokong lengai, yang mana tiub kaca Pyrex telah digunakan.

TABLE OF CONTENTS

Page

LIST OF TABLES

LIST OF FIGURES

LIST OF APPENDICES

ABBREVIATION AND SYMBOLS

Abs	Absorbance
AC	Activated carbon
AOPs	Advanced oxidation processes
GAC	Granular activated carbon
M-TiO_2	Metal-doped TiO_2
TiO_2-GAC	TiO_2 coated on granular activated carbon
M-TiO_2-GAC	Metal-doped TiO_2 coated on granular activated carbon
MB	Methylene blue
MO	Methyl orange
UV	Ultra-Violet
TiO_2	Titanium dioxide
e_{CB}^{-}	Conduction band electron
h_{VB}^{+}	Valence band hole
λ_{max}	Maximum absorbance
k_1	pseudo-first order kinetic rate constant
BET	Brunauer-Emmet-Teller
SEM	Scanning Electron Micrograph
XRD	X-Ray Diffractogram
% removal	Percentage of MB removal

CHAPTER 1

INTRODUCTION

1.1 An Overview of Advanced Oxidation Processes in Wastewater Treatment

Industrial, agricultural and municipal wastewaters can contain either inorganic (e.g. heavy metals, acids) or organic (e.g. dyes, surfactants, oils, pesticides) pollutants, or a combination of both types of pollutants. The composition of wastewaters, however depends on the type of sources. Continuous discharge of untreated or poorly treated wastewaters into the aquatic environment can cause adverse impacts (Sasawsky *et al.*, 2000; Driscoll *et al.*, 2003). Inputs of the pollutants can lead to degradation in water quality besides causing ecological and health impacts. It is therefore necessary to treat these wastewaters to remove the pollutants prior to discharge. In many countries, such discharges need to attain specific standards in accordance with the environmental regulation. In Malaysia, this requirement is specified under the Environmental Quality Act 1974, specifically under the Environmental Quality (Sewage and Industrial Effluents) Regulations 1979.

A number of physical, biological and chemical methods are available for wastewater treatment. Advanced oxidation processes (AOPs) is one of the chemical methods. This technique have been widely used to treat organic and inorganic pollutants in wastewater, sludge and air (Fujishima *et al.*, 2000; Tan *et al.*, 2003; Charatterjee and Dasgupta, 2005). AOPs use the combination of powerful oxidizing agents and UV light to photodegrade pollutants (Hsing *et al.*, 2007; Malato *et al.*, 2007). AOPs rely mainly on the formation of reactive and short-lived oxygen containing intermediates such as hydroxyl radicals ($HO^{\bullet}$) and superoxide radicals ($O_2^{\bullet-}$) which are responsible in the decomposition of pollutants (Yang *et al.*, 2004c; Haque and Muneer, 2007). The pollutants are degraded into CO_2, water and mineral-end products such as NH_4^+, NO_3^- and SO_4^{2-} (Anpo and Takeuchi, 2003; Konstantinou and Albanis, 2004; Kumar *et al.*, 2005).

Over the years AOPs have undergone significant developments. Starting with the basic process of oxidation in the presence of H_2O_2 and UV, AOPs have evolved to photooxidation involving TiO_2 photocatalyst (Dvoranová *et al.*, 2002; Bahnemann, 2004; Coleman *et al.*, 2005). The TiO_2 photocatalyst used are in the form of suspension (as powdered form) or thin films. Subsequently, metal-doped TiO_2 photocatalysts were introduced. Lately, there have been increasing interests on TiO_2 photocatalyst immobilized on activated carbon adsorbent (Carp *et al.*, 2004; Subramani *et al.*, 2007).

Much of current researches on AOPs are focused on photocatalysis involving TiO_2. In general, TiO_2 is photoactive under UV light shorter than 400 nm (Agustina *et al.*, 2005; Liu *et al.*, 2008). Under this condition, TiO_2 generates electron-hole pairs, namely electron from conduction band (e_{CB}^-) and hole at valence band (h_{VB}^+), which subsequently react with H_2O or O_2 to generate the reactive radicals $HO^\bullet$, $O_2^{\bullet-}$ and $HO_2^\bullet$ (Malato *et al.*, 2002; Witmann *et al.*, 2005). Under normal temperature and air pressure, TiO_2 systems in the presence of UV-irradiation could completely degrade most pollutants to harmless compounds (Lu *et al.*, 2008). However, the degradation is more effective in the presence of H_2O_2 (Kiwi *et al.*, 1993; Halmann, 1996; Oppenländer, 2003).

Studies have also been carried out for the photocatalytic degradation process involving single or multi metal-doped TiO_2 (Yang *et al.*, 2002; Arabatzis *et al.*, 2003; Park *et al.*, 2004; Yang *et al.*, 2004b; Liu *et al.*, 2006a). The transition metals with many valencies are most frequently studied. The metal dopants can be *p*-Type (valencies lower that Ti^{4+}) or *n*-Type (valencies higher than Ti^{4+}). Examples of *p*-Type dopants include Cu^{2+}, Fe^{3+}, Ni^{2+} and Zn^{2+}ions, whilst *n*-Type dopants are V^{5+}, W^{6+}, Nb^{5+} and Mo^{5+} ions (Carp *et al.*, 2004; Park *et al.*, 2004; Li *et al.*, 2007c).

TiO_2 photocatalyst was initially used as suspension in slurry systems (Carp *et al.*, 2004). Due to the problem associated with the need of eventual separation by filtration during post treatment, it is now used in the form of thin films (Alam and Cameron, 2001; Gao and Liu, 2005; Yuan *et al.*, 2007). Recently, instead of the conventional Pyrex-glass tubes, specific adsorbents were used as support for the thin films. Examples of adsorbents include zeolites, silica, alumina, clay and activated carbon (Carp *et al.*, 2004; Moriguchi *et al.*, 2004; Crini, 2006; Li *et al.*, 2007b; Subramani *et al.*, 2007). Studies using activated carbon as support have reported better photocatalytic degradation compared to conventional TiO_2 thin films (El-Sheikh *et al.*, 2004; Carpio *et al.*, 2005; Liu *et al.*, 2006c; Zhang *et al.*, 2006b; Matos *et al.*, 2007).

The TiO_2 thin film can be prepared according to several methods such as chemical vapour deposition, physical vapour deposition, spray pyrolysis and sol-gel techniques. Each method has it's own advantages and disadvantages (Sonawane *et al.*, 2004, Carp *et al.*, 2004). The sol-gel dip-coating method is one of the preferred sol-gel techniques (Sonawane *et al.*, 2004; Du *et al.*, 2005). Sol-gel techniques normally are lower in equipment cost, and can be used to prepare thin films with good homogeneity and at low process temperature (Dong *et al.*, 2002; Zhou, *et al.*, 2004).

1.2 Wastewater Treatment by Metal Doped-Titania-Assisted Oxidation Process

There have been a number of studies involving wastewater treatment using TiO_2 and metal-doped TiO_2. Some studies reported that metal-doped TiO_2 produced enhanced photocatalytic degradation of pollutants (Arabatzis *et al.*, 2003; Xu *et al.*, 2004; Yang *et al.*, 2004b; Wu *et al.*, 2006), while some reported poor or reduction in photocatalytic activity (Matos *et al.*, 2001; Kemp and McIntyre, 2006). Similar to undoped TiO_2, the photocatalytic efficiency of the metal-doped TiO_2 photocatalysts also can be influenced by factors such as type of metal dopant, metal to Ti ratio, solution pH, catalyst's concentration, pollutant type, addition and concentration of oxidant (Lee *et al.*, 2004; Li and Li, 2002a; Li *et al.*, 2005a; Senthilkumaar *et al.*, 2006; Zhu *et al.*, 2006a).

The addition of metal dopant into TiO_2 can modify the morphology, chemical environment and distribution of the TiO_2 thin films (Arroyo *et al.*, 2002). Metal-doped TiO_2 can also exhibit photocatalytic characteristics under visible light, with

25-32% of solar light absorption (Dvoranová *et al.*, 2002; Teoh *et al.*, 2007). However, it is not as effective as under UV light irradiation (Fujishima and Zhang, 2006).

Both *n*-Type and *p*-Type metal dopants can enhance the photocatalytic activity of TiO_2 (Li and Li, 2002b; Park *et al.*, 2004; Yang *et al.*, 2004b; Xin *et al.*, 2007). However, its' photocatalytic efficiency can be influenced by the concentration of metal-dopant (i.e. the metal to Ti ratio). For example, Yang *et al.* (2004b) showed that the photocatalytic degradation rate constant of methyl orange (MO) by molybdenum-doped TiO_2 increased to 0.054 min^{-1} from 0.028 min^{-1} with increase in Mo concentration from 0 to 1 mol%. The rate, however, dropped when Mo content exceeded 1 mol% (i.e. 0.03 min^{-1} at 1.5 mol %). The optimum metal to Ti ratio, however, can vary according to the type of pollutant. For example, the photocatalytic degradation of XRG yellow dye is most effective when 0.40% Fe^{3+}-doped TiO_2 was used (Zhu *et al.*, 2006a) while the degradation of methyl orange (MO) is effective using 4% Fe^{3+}-doped TiO_2 (Sonawane *et al.*, 2004).

There have been few researches on photocatalysis using multi-metal-doped TiO_2 (Yang *et al.*, 2002; Zhang *et al.*, 2006a; Xu *et al.*, 2008). The synergistic effect between the metal dopants can enhance the photocatalytic efficiency of TiO_2. However, the metal to Ti ratio can significantly affect the efficiency of multi metal-doped TiO_2. For example, TiO_2 co-doped with Fe^{3+} and Eu^{3+} ions at appropriate ratios, namely 1% Fe^{3+} and 0.5% Eu^{3+}, shows superior photocatalysis to degrade chloroform in solution compared to undoped TiO_2 (Yang *et al.*, 2002). Low or excessive ratio of metal dopants, however, can significantly retard the photocatalytic reactivity (Carp *et al.*, 2004).

The addition of oxidants such as H_2O_2 can enhance the photocatalytic activity of metal-doped TiO_2 catalysts (Senthilkumaar *et al.*, 2005; Haque and Muneer, 2007). However, excessive H_2O_2 can decrease the rate of photocatalytic degradation (Fernández *et al.*, 2004; Tryba *et al.*, 2006).

As with undoped TiO_2, most studies on photocatalytic degradation using metal-doped TiO_2 involved the catalyst being coated as thin films on inert supports namely Pyrex-glass, soda lime glass, fiberglass and glass sheets (Sonawane *et al.*, 2004; Du *et al.*, 2005; Thevenet *et al.*, 2005). Unlike undoped TiO_2, there have been only a few reports on catalysis involving metal-doped TiO_2 coated on adsorbent materials such as activated carbon (Zhang *et al.*, 2005a; Sun *et al.*, 2006). For example, Sun *et al.* (2006) reported that Sn(IV)/TiO_2/AC produced greater degradation of Orange G (~2x) as compared with TiO_2/AC. Meanwhile, Zhang *et al.* (2005a) reported that the degradation of methyl orange (MO) using Ag-doped TiO_2/AC is at least 1.25x higher than pure TiO_2 and Degussa P25.

1.3 Objectives of the Research

This research focuses on photocatalytic degradation of an organic pollutant using metal-doped TiO_2 coated on different support materials, namely Pyrex-glass tube and granular activated carbon (GAC). Methylene blue (MB) was used as the simulated/synthetic pollutant in aqueous solution. The objectives of this research are:

a) To prepare metal-doped TiO_2 catalyst according to simple sol-gel dip-coating method;

b) To determine the photocatalytic degradation of MB in the presence of metal-doped TiO_2 coated on Pyrex-glass tube;

c) To compare MB degradation by metal-doped TiO_2 and undoped TiO_2;

d) To compare the photocatalytic degradation of MB in the presence of single-metal-doped TiO_2 and dual-metals-doped TiO_2;

e) To determine the photocatalytic degradation of MB in the presence metal-doped TiO_2 coated on GAC.

1.4 Scope of Study

This study investigated the photocatalytic degradation of MB by metal-doped TiO_2 in the presence of UV and H_2O_2. The metal-doped TiO_2 were prepared as thin films on Pyrex-glass tubes by sol-gel dip-coating method. The metal dopants used were *n*-Type (Cr^{3+}, Cu^{2+}, Fe^{3+}) and *p*-Type (Mo^{5+} and V^{5+}). The metal-doped TiO_2 catalysts were single-metal-doped TiO_2 (Cr^{3+}-TiO_2, Cu^{2+}-TiO_2, Fe^{3+}-TiO_2, Mo^{5+}-TiO_2, V^{5+}-TiO_2) and dual-metal-doped TiO_2 (Cr^{3+}-Mo^{5+}-TiO_2, Cr^{3+}-V^{5+}-TiO_2, Cu^{2+}-Mo^{5+}-TiO_2, Cu^{2+}-V^{5+}-TiO_2, Fe^{3+}-Mo^{5+}-TiO_2, Fe^{3+}-V^{5+}-TiO_2, Mo^{5+}-V^{5+}-TiO_2). The photocatalytic degradation was also determined using metal-doped TiO_2 coated as thin films on granular activated carbon, M-TiO_2/GAC, where M-TiO_2 is the metal-doped TiO_2 catalyst (i.e. V^{5+}-TiO_2) with the best degradation rate obtained in the earlier experiments. Comparison was made with undoped TiO_2, TiO_2-GAC and GAC systems. The performances of these titania assisted systems in photocatalytic degradation of MB in aqueous solution were evaluated based on the changes in absorbance values at λ_{max}= 665 nm.